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(19)

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(54) CURABLE POLYMER POWDER COATING COMPOSITIONS

(71) We, BAYER AKTIENGESELLSCHAFT of 509 Leverkusen, Germany, a body corporate organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to novel curable polymer powder coating powders compositions comprising a mixture of a *bis-* or *tris-*(5,6 - dihydro - 4H - 1,3 - oxazine) and a polymer containing carboxylic acid groups. These powders are suitable for use in the electrostatic powder-spraying process.

Binders for use in electrostatic powder spraying should be brittle, readily powdered resins in their uncross-linked form, which, as powders, remain free-flowing and do not lump at temperatures of up to 50°C. Following electrostatic application to the substrate, the powders should level out smoothly at temperatures in the range of from 80 to 120°C and they should bake to form insoluble, infusible coatings at temperatures above 130°C. The powders must also be able to take an electrostatic charge and hold this charge after application to metal articles for a sufficient length of time until they are baked. In addition, such binders should not prematurely crosslink near their levelling temperature because, in general, they are mixed with pigments, catalysts and levelling agents in the melt at temperatures of approximately 100°C. In cases where an external crosslinking agent is used, as in the process according to the invention, the component which acts as the crosslinking agent should melt at a temperature at which the resin also melts and should be compatible and homogeneously miscible with the resin. When the mixture hardens, the crosslinking agent which has been added should not affect the storage properties of the mixture at temperatures of up to 50°C, and the system should not disintegrate on cooling. After levelling and baking, the compatible mixture of crosslinking agent and resin should give a high-gloss, weather resistant coating which is unaffected by chemicals and by solvents.

Powder lacquers based on polyepoxides are known and these satisfy most of the requirements referred to above, although their resistance to weathering is inadequate for a number of applications. The inadequate weathering resistance of epoxide powder lacquers has prompted industry to develop powder lacquers based on polyacrylates. Such polyacrylate powder lacquers are described, for example, in French Patent Specification No. 2,035,185. These resins contain methylmethylol ether groups which are firmly anchored in the polymer and which allow thermal crosslinking. Unfortunately, such resins show inadequate stability in storage at elevated temperatures of the kind which can occur in particular during transportation in Southern countries. The resins generally begin to lump at temperatures as low as 40° and thereafter are no longer free-flowing. Permanent free-flow properties are, however, essential to any powder-application process.

The crosslinkable coating mixtures in powder form according to the invention effectively satisfy the aforementioned requirements for electrostatic powder spraying.

Accordingly, the invention provides curable coating powders suitable for the electrostatic powder-spraying process, comprising a powdered mixture of:

(A) a copolymer (as hereinafter defined) comprising copolymerised units of:

I. from 25 to 70% by weight of styrene, α - methylstyrene, *o* - chlorostyrene, *p* - chlorostyrene, *p* - tert. - butyl-

styrene, acrylonitrile, methacrylonitrile or a mixture of two or more thereof;

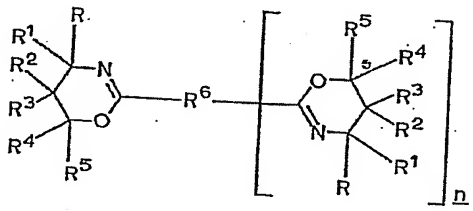
II. from 30 to 65% by weight of an acrylic acid ester having from 1 to 12 carbon atoms in the alcohol radical or a methacrylic acid ester having from 2 to 12 carbon atoms in the alcohol radical, or a mixture of two or more thereof;

III. from 0 to 25% by weight of methyl methacrylate; and

IV. from 5 to 20% by weight of acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, crotonic acid, or a mixture of two or more thereof,

the sum of the percentages of the components I to IV being 100 and the average molecular weight being in the range of from 3000 to 20,000,

(B) at least one *bis*- or *tris* - (5,6 - dihydro - 4H - 1,3 - oxazine) of the general formula:



in which

n is 1 or 2,

R, R^1, R^2, R^3, R^4 and R^5 are the same or different and each represents a hydrogen atom or a hydrocarbon radical having from 1 to 6 carbon atoms; and

R^6 represents a bond (*n* being 1) or (*n* being 1 or 2) a cycloaliphatic hydrocarbon di- or tri - valent radical having from 3 to 10 carbon atoms; an optionally partially unsaturated alkylene di- or tri - valent radical having from 1 to 18 carbon atoms which may optionally contain one or more aromatic hydrocarbon radicals having from 6 to 10 carbon atoms or one or more heterocyclic radicals having from 5 to 14 carbon atoms; a di- or tri - valent radical comprising one or more optionally substituted aromatic hydrocarbon radicals having from 6 to 12 carbon atoms; or a heterocyclic di- or tri - valent radical having from 5 to 14 carbon atoms, and

(C) optionally additives such as pigments and levelling agents, the mixture containing, on a basis of 100 parts by weight total, from 5 to 25 parts by weight of the *bis*- or *tris* - (5,6 - dihydro - 4H - 1,3 - oxazine) (B) to from 95 to 75 parts by weight of the acrylic resin (A), and up to 150% by weight, based on (A) and (B) of one or more pigments and from 0.1 to 5% by weight, based on (A), of a levelling agent.

The powders according to the invention remain free-flowing at temperatures above 50°C, they preferably have a grain size in the range of from 30 to 120 μ and they have the advantage of not giving off any volatile constituents during baking.

The following poly - (5,6 - dihydro - 4H - 1,3 - oxazines) are mentioned as specific examples:

1,3- and 1,4 - *bis* - (5',6' - dihydro - 4'H - 1',3' - oxazin - 2' - yl) - benzene; 1,3- and 1,4 - *bis* - (5',5' - dimethyl - 5',6' - dihydro - 4'H - 1',3' - oxazin - 2' - yl) - benzene; 1,3- and 1,4 - *bis* - (6' - methyl - 5',6' - dihydro - 4'H - 1',3' - oxazin - 2' - yl) - benzene; 1,3,5 - *tris* - (5,6 - dihydro - 4'H - 1',3' - oxazin - 2' - yl) - benzene; 2,6- and 3,5 - *bis* - (5',6' - dihydro - 4'H - 1',3' - oxazin - 2' - yl) - pyridine; 2,2' - *bis* - (5,6 - dihydro - 4H - 1,3 - oxazine); 1,2 - *bis* - (5',6' - dihydro - 4'H - 1',3' - oxazin - 2' - yl) - ethane; 1,4 - *bis* - (5',6' - dihydro - 4'H - 1',3' - oxazin - 2' - yl) - butane; 4,4' - *bis* - (5'',6'' - dihydro - 4''H - 1'',3'' - oxazin - 2'' - yl) - diphenyl methane; 4,4' - *bis* - (5'',6'' - dihydro - 4''H - 1'',3'' - oxazin - 2'' - yl) - diphenyl oxide.

The poly - (5,6 - dihydro - 4H - 1,3 - oxazines) used can be prepared by the methods described in German Offenlegungsschrift 21 53 513.

The copolymers containing carboxyl groups comprise copolymerised units of the following monomers:

I. styrene, methyl styrene, α - methyl styrene, *p* - tert. - butyl styrene, *o* - chlorostyrene, *p* - chlorostyrene, acrylonitrile or methacrylonitrile, preferred are styrene and/or α - methyl styrene;

II. acrylic acid esters having from 1 to 12 carbon atoms in the alcohol component and/or methacrylic acid esters having 2 to 12 carbon atoms in the alcohol component, preferred said esters having up to 8 carbon atoms in the alcohol component;

III. methyl methacrylate and

IV. acrylic acid, methacrylic acid, crotonic acid, maleic acid, fumaric acid, or itaconic acid, preferred acrylic and/or methacrylic acid.

In the context of the invention, the term copolymer includes not only copolymers of the specified composition, but also mixtures of copolymers, providing that the mixtures are prepared in such a way that the overall composition lies within the ranges mentioned above.

The copolymers are prepared by conventional methods of bulk, solution, dispersion

and bead polymerisation, preferably by solution or bulk polymerisation. Methods of this kind are described for example in "Methoden der Organischen Chemie", Houben-Weyl, 4th Edition, Vol. 14/1, pages 24—556 (1961).

In cases where the polymerisation is carried out in solution, solvents such as methylene chloride, ethanol, *iso* - propanol, *n* - propanol, *n* - butanol, *iso* - butanol, *tert.* - butanol, acetic acid methyl-to-butyl esters, acetone, methylethyl ketone, benzene, toluene, etc. may be used.

The polymerisation reactions are preferably carried out at temperatures of from 40 to 180°C.

Examples of suitable initiators include percarbonates; peresters, such as *tert.* - butyl perpivalate or peroctoate; benzoyl peroxide; *o* - methoxy benzoyl peroxide, dichlorobenzoyl peroxide; and azodiisobutyrodinitrile; and are used in quantities of from 0.5 to 3% by weight, based on monomer.

Conventional molecular weight regulators, such as thioglycol, thioglycerin or *tert.* - dodecyl mercaptan, can also be used.

The copolymer solution is freed from the solvent in suitable apparatus, preferably in evaporator screws, at temperatures of from 90 to 180°C, for example by the process described in German Offenlegungsschrift No. 20 05 691, cooled, granulated and ground.

Isolation can, however, also be carried out by other methods, for example by spray drying, by removing the solvent with steam or by precipitation with water from a water-miscible solvent.

After isolation, the copolymers can be mixed with up to 150% by weight, based on copolymer, preferably up to 100% by weight, of inorganic or organic pigments, at temperatures of from 80 to 120°C. The following are mentioned as examples of pigments: titanium dioxide, iron oxides, chromium oxide, lead chromates, cadmium sulphide, carbon black, aluminium and copper bronze, phthalocyanine and azo dyes.

The melts can also have added to them from 0.1 to 5% by weight, based on copolymer, of levelling agents such as silicones, poly - 2 - ethyl - hexylacrylate, polybutyl acrylate or their copolymers and cellulose derivatives; and catalysts such as organic and inorganic acids, tertiary amines, dicyanodiamide and tin compounds. Fillers, such as barium sulphate, aluminium oxide or tin oxide, may also optionally be added to the melts.

It is of course also possible to add pigments and levelling agents to the monomers before polymerisation or, in the event of solution polymerisation, to the copolymer solution before removal of the solvent.

The *bis*- or *tris* - (5,6 - dihydro - 4H - 1,3 - oxazine) is preferably mixed in together with the pigments, levelling agents and catalysts in a mixing screw at a temperature of from 80 to 120°C. The mixing times are preferably from about 1 minute to 10 minutes. Mixing for periods longer than this results in precrosslinking in the product. Under these conditions, a homogeneous mixture is formed, which does not disintegrate even when cooled.

The solvent-free, optionally pigmented mixtures which are brittle after cooling in their uncrosslinked state are ground to a fine grain size of preferably from 30 to 120 μ and optionally graded according to grain size.

The polymer powders used in accordance with the invention remain free-flowing at temperatures above 50°C, preferably above 60°C, having levelling temperatures of from about 80 to 120°C and being baked over periods of from 3 to 30 minutes at temperatures from 130°C to 220°C, preferably at temperatures of from 160 to 200°C, accompanied by crosslinking.

The polymer powders have average molecular weights of from 3000 to 20,000, preferably from 3000 to 10,000, as measured in an organic solvent such as acetone by the reduction in vapour-pressure method.

The powders may be applied to suitable substrates, especially metals by conventional electrostatic powder spraying methods (40 to 90 kV). *cf.* D. R. Davis "Coating with Electrostatic Dry-spray" in Plastics Technology, June 1962, pages 37—38.

The baked films (thickness from 40 to 300 μ) of the polymer powders used in accordance with the invention show outstanding bond strength and hardness coupled with elasticity. They are also distinguished by their high gloss and outstanding weather resistance.

The powders may be used for coating domestic appliances, metal components in vehicle building, metal components which are severely exposed to weathering such as motor vehicle bodywork, fascade panels, tubes and wire netting, and for coating tools for use in forestry and agriculture.

EXAMPLE 1

a) Preparation of the polymer

8 kg of a monomer mixture, comprising 50 parts by weight of styrene, 35 parts by weight of butyl acrylate, 15 parts by weight of acrylic acid, 1 part by weight of *tert.* - dodecyl mercaptan and 0.005 part by weight of hydroquinone, were heated under nitrogen in a 40-litre-capacity mixer vessel until a gentle reflux occurred. The temperature was adjusted to 130 to 140°C. A cooled mixture of 15 g of *tert.* - butyl perpivalate in petrol fraction ($b.p._{760}$ 70—130°C) and 640 g of the monomer mixture was introduced into the initial monomer mixture and polymerised with it over a period of 1 hour. Thereafter, the solids content was 80% (determined by concentrating a sample by evaporation for 30

minutes at 250°C). The introduction of the initiator could be restricted or stopped if the reaction became too violent.

A mixture of 16 kg of monomer mixture and 160 g of *tert.* - butyl perpivalate (the components being mixed shortly before introduction in a vessel cooled with brine) was introduced into the melt at a temperature of 140 to 145°C over a period of 3 hours and the resulting reaction mixture was heated to a temperature of 160°C after the reaction had ceased. 180 g of di - *tert.* - butyl peroxide and 180 g of monomer mixture were then added dropwise over a period of a further hour. The volatile constituents (catalyst decomposition products and monomer impurities) were then distilled off and the temperature was subsequently maintained at 170°C for 2 hours. This was followed by brief degassing *in vacuo* and the melt was then run off. The lacquer formed from the melt had a melting point of 95°C and could be converted into a powder without lumping. The average molecular weight was approximately 6000, as measured by the osmometry method in acetone. The copolymer contained approximately 50.0% by weight of styrene, approximately 15% by weight of acrylic acid and approximately 35% by weight of butyl acrylate.

b) Preparation of the lacquer powder

A mixture of 100 parts by weight of a polyacrylate prepared as described in a), 20 parts by weight of 1,4 - *bis* - (5',6' - dihydro - 4'H - 1',3' - oxazin - 2' - yl) - benzene and 60 parts by weight of titanium dioxide (rutile type) was prepared in an extruder. The residence time in the extruder was about 30 seconds at a temperature of 100 to 110°C.

After cooling, the extruded mixture was ground and sifted. The fraction having grain sizes of less than 80 μ could be stored almost indefinitely at 50°C without lumping and it had the requisite free-flow properties. The powder mixture was applied to degreased metal panels by means of a conventional spray gun. The particles were negatively charged with respect to the panel, the voltage applied being 60 kV.

The coatings were baked for 30 minutes at 180°C and a scratch-resistant, elastic film was obtained which was unaffected by solvents.

A 70 μ thick film gave the following test results:

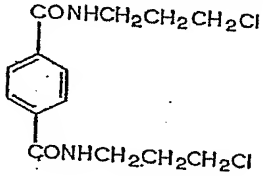
Erichsen-indentation according to DIN 53 156	9.5 mm
Lattice cut according to DIN 53 151	GT 1
Mandrel-bending test according to Gardner	2 mm
Gloss measurement according to ASTM D 523 (<60°C)	90%
Short-term weathering in a Sunshine weatherometer:	incipient chalking after 600 hours

The 1,4 - *bis* - (5',6' - dihydro - 4'H - 1',3' - oxazin - 2' - yl) - benzene was prepared as follows:

1,430 g (12 mols) of thionyl chloride were introduced dropwise at 80°C into a suspension of 1,500 g (5.36 mols) of terephthalic acid - *bis* - (3 - hydroxypropylamide) (Plaste und Kautschuk 7,372 (1959); m.p. 213°C) in 3 litres of dry benzene over a period of 7 hours. After the evolution of gas had ceased, the mixture was refluxed for 15 hours. The suspension was filtered off under suction and the resulting filter cake was washed with benzene and dried in vacuo at 40°C.

Yield: 1,607 g (94% of the theoretical yield) of terephthalic acid - *bis* - (3 - chloropropyl amide); m.p. 212°C.

$C_{16}H_{20}Cl_2N_2O_2$ (molecular weight 317)

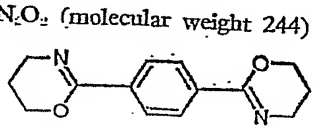


Calculated:
C 53.9% H 5.7% Cl 22.4% N 8.8%
O 10.1%
Found:
C 52.8% H 5.9% Cl 22.1% N 8.8%
O 10.5%

159 g (0.5 mol) of terephthalic acid - *bis* - (3 - chloropropylamide) were stirred with 276 g (2 mols) of potassium carbonate in 600 ml of dimethyl formamide at 130°C for 4 hours. Inorganic salts were separated off by hot filtration under suction. The filtrate was allowed to cool and the precipitated crystalline product was isolated therefrom. A second fraction was obtained from the concentrated mother liquor.

Yield: 101 g (83% of the theoretical yield) of 1,4 - *bis* - (5',6' - dihydro - 4'H - 1',3' - oxazin - 2' - yl) - benzene; m.p. 220—222°C.

$C_{14}H_{16}N_2O_2$ (molecular weight 244)



Calculated:
C 68.9% H 6.5% N 11.5% O 13.1%
Found:
C 68.6% H 6.5% N 11.4% O 13.4%

EXAMPLE 2

A mixture of:

100 parts by weight of a polyacrylate prepared as described in Example 1 a);
20 parts by weight of 1,3 - *bis* - (5',6' - dihydro - 4'H - 1',3' - oxazin - 2' - yl) - benzene;
60 parts by weight of titanium dioxide (rutile); and
2 parts by weight of the levelling agent consisting of a copolymer of 70% by weight of 2 - ethylhexyl acrylate and 30% by weight of ethyl acrylate was prepared in an extruder.

The residence time in the extruder was 30 seconds at a maximum temperature of 110°C. The solid mixture obtained was ground and sifted to grain sizes of less than 80 μ and remained free-flowing after storage at 50°C for 24 hours. The powder was electrostatically applied to metal panels as described in Example 1 and baked at 180°C and 190°C. The following results were obtained on 60 μ thick films:

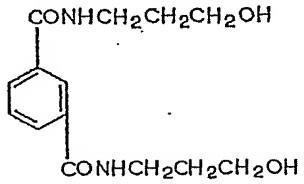
Baking time	30 mins at 180°C	15 mins at 190°C	30 mins at 190°C
Erichsen indentation according to DIN 51 156	9.3 mm	9.5 mm	9.5 mm
Lattice cut according to DIN 53 151	GT 1	GT 1	GT 1
Mandrel-bending test according to Gardner	2 mm	2 mm	2 mm
Gloss measurement according to ASTM D 523 (∢60°C)	90%	95%	95%

The 1,3 - *bis* - (5',6' - dihydro - 4'H - 1',3' - oxazin - 2' - yl) - benzene was prepared as follows:

23 g of methanol were distilled off on a falling condenser from a mixture of 97 g (0.5 mol) of isophthalic acid dimethyl ester and 113 g (1.5 mols) of 3 - amino - 1 - propanol in a bath heated to 140°C over a period of 1.5 hours. The crystalline residue was recrystallised from 250 ml of methanol.

Yield: 110 g (78% of the theoretical yield) of isophthalic acid - *bis* - (3 - hydroxy - propylamide); m.p. 120—122°C.

$C_{14}H_{20}N_2O_4$ (molecular weight 280)



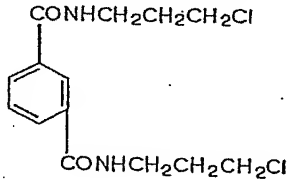
Calculated:
C 60.0% H 7.2% N 10.0% O 22.8%
Found:
C 59.7% H 7.3% N 10.2% O 23.1%

27 g (0.22 mol) of thionyl chloride were introduced dropwise at 80°C into a solution of 28 g (0.1 mol) of isophthalic acid - *bis* - (3 - hydroxypropyl amide) in 150 ml of dry benzene.

Stirring was continued until the evolution of gas had ceased, the precipitated semi-solid product was filtered off under suction and recrystallised from xylene.

Yield: 23 g (73% of the theoretical yield) of isophthalic acid - *bis* - (3 - chloropropyl amide); m.p. 119°C.

$C_{14}H_{18}Cl_2N_2O_2$ (molecular weight 317)

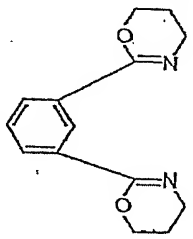


Calculated:
C 53.0% H 5.7% Cl 22.4% N 8.8%
O 10.1%
Found:
C 53.6% H 5.7% Cl 22.4% N 8.7%
O 10.3%

15.9 g (0.05 mol) of isophthalic acid - *bis* - (3 - chloropropylamide) were stirred with 69 g (0.5 mol) of potassium carbonate in 100 ml of dimethyl formamide at 130°C for 10 hours. Inorganic salts were separated by hot filtration under suction and the filtrate concentrated *in vacuo*. The residue obtained from this concentrate was recrystallised from cleaning spirit.

Yield: 8.1 g (66% of the theoretical) of 1,3 - *bis* - (5',6' - dihydro - 4'H - 1',3' - oxazin - 2' - yl) - benzene; m.p. 84°C.

$C_{14}H_{16}N_2O_2$ (molecular weight 244)



Calculated:
C 68.9% H 6.5% N 11.5% O 13.1%
Found:
C 68.4% H 6.5% N 11.3%

EXAMPLE 3

An acrylate resin with a measured molecular weight of approximately 5000 was prepared by the polymerisation process described in Example 1 from 35% by weight of butyl acrylate, 25% by weight of styrene, 10% by weight of methacrylic acid butyl ester, 15% by weight of methacrylic acid methyl ester and 15% by weight of acrylic acid.

100 parts by weight of the polymer were homogenised in an extruder with 15 parts by weight of 1,4 - *bis* - (5',6' - dihydro - 4'H - 1',3' - oxazin - 2' - yl) - benzene and 60 parts by weight of titanium dioxide (rutile). The residence time in the extruder was 20 seconds at a maximum temperature of 110°C. The mixture was worked up as described in Example 1 into a powder which could be stored without lumping at 55°C for at least 48 hours. The powder was applied electrostatically to metal panels and the coatings were baked at 180°C for 30 minutes.

The following test results were obtained from 70 μ thick films:

Erichsen indentation according to DIN 53 156	9.0 mm
Lattice cut according to DIN 53 151	GT 1
Mandrel-bending test according to Gardner	4 mm
Gloss measurement according to ASTM D 523 (∢60°C)	90%
Short-term weathering in a Sunshine weatherometer:	incipient chalking after 750 hours

EXAMPLE 4

A powdered mixture was prepared as described in Example 1 with the exception that equal parts by weight of 1,3,5 - *tris* - (5',6' - dihydro - 4'H - 1',3' - oxazin - 2' - yl) - benzene were used instead of the 1,4 - *bis* - (5',6' - dihydro - 4'H - 1',3' - oxazin - 2' - yl) - benzene. A powder was obtained which could be stored indefinitely at 50°C. This powder gave thoroughly crosslinked, hard high-gloss films after being fired at 180°C for 30 minutes.

The 1,3,5 - *tris* - (5',6' - dihydro - 4'H - 1',3' - oxazin - 2' - yl) - benzene was prepared as follows:

1,3,5 - *tris* - (5',6' - dihydro - 4'H - 1',3' - oxazin - 2' - yl) - benzene

49 g of methanol were distilled off on a falling condenser from a mixture of 151 g (0.6 mol) of benzene - 1,3,5 - tricarboxylic acid trimethyl ester and 202 g (2.7 mol) of 3 - amino - 1 - propanol over a period of 2 hours at a bath temperature of 140°C. The waxy residue was digested with acetone and the crystalline residue was recrystallised from a mixture of 600 ml of methanol and 1300 ml of acetone.

Yield: 167 g (73% of the theoretical) of benzene - 1,3,5 - tricarboxylic acid - *tris* - (3' - hydroxypropyl amide) m.p. 167°C.

$C_{18}H_{27}N_3O_6$ (molecular weight 381).
Calculated:
C 56.7% H 7.1% N 11% O 25.2%
Found:
C 57.1% H 7.2% N 11.1% O —

64 g (0.54 mol) of thionyl chloride were introduced dropwise at 80°C into a suspension of 57 g (0.15 mol) of benzene - 1,3,5 - tricarboxylic acid *tris* - (3' - hydroxypropyl amide) in 250 ml of dry benzene. The mixture was stirred at 80°C until the evolution of gas had ceased, after which the solid phase was isolated by filtration and recrystallisation from a little amount of ethanol.

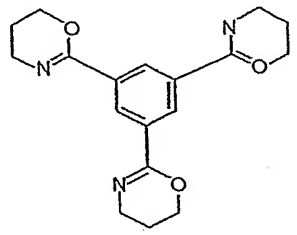
Yield: 44 g (67% of the theoretical) of benzene - 1,3,5 - tricarboxylic acid - *tris* - (3' - chloropropyl amide); softening point 65°C, $C_{15}H_{24}Cl_3N_3O_3$ (molecular weight 436.5).

Calculated: Cl 24.4%
Found: Cl 24.4%

39.9 g (0.09 mol) of benzene - 1,3,5 - tricarboxylic acid - *tris* - (3' - hydroxypropyl amide) and 124 g (0.9 mol) of potassium carbonate were heated with stirring at 130°C in 200 ml of dimethyl formamide for 10 hours. Inorganic salts were isolated by filtration at 90°C, the filtrate was left to cool and the product which precipitated from the filtrate was recrystallised from methanol.

Yield: 27 g (90% of the theoretical) of 1,3,5 - *tris* - (5',6' - dihydro - 4'H - 1',3' - oxazin - 2' - yl) - benzol; m.p. 312°C., (decomposition; quickly heated).

$C_{18}H_{21}H_3O_3$ (molecular weight 327)



Calculated:
C 66.0% H 6.5% N 12.8% O 14.7%
Found:
C 65.6% H 6.6% N 12.8% O —

WHAT WE CLAIM IS:—

1. A curable coating composition comprising a powdered mixture of:

(A) a copolymer (as hereinbefore defined) comprising copolymerised units of:

I. from 25 to 70% by weight of styrene, α - methylstyrene, *o* - chlorostyrene, *p* - chlorostyrene, *p* - tert. - butyl styrene, (meth)acrylonitrile or a mixture of two or more thereof;

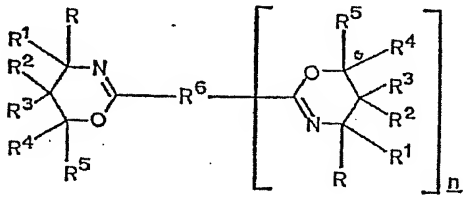
II. from 30 to 65% by weight of an acrylic acid ester having from 1 to 12 carbon atoms in the alcohol radical or a methacrylic acid ester having from 2 to 12 carbon atoms in the alcohol radical, or a mixture of two or more thereof;

III. from 0 to 25% by weight of methyl methacrylate; and

IV. from 5 to 20% by weight of acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, crotonic acid, or a mixture of two or more thereof,

the sum of the percentage components I to IV being 100% and the average molecular weight being from 3000 to 20,000; and

(B) one or more *bis*- or *tris* - (5,6 - dihydro - 4H - 1,3 - oxazines) of the general formula:



in which

n is 1 or 2,

R, R^1, R^2, R^3, R^4 and R^5 are the same or different and each represents a hydrogen atom or a hydrocarbon radical having from 1 to 6 carbon atoms; and

R^6 represents a bond (*n* being 1) or (*n* being 1 or 2) a cycloaliphatic hydrocarbon di- or tri - valent radical having from 3 to 10 carbon atoms; an optionally partially unsaturated alkylene di- or tri - valent radical having from 1 to 18 carbon atoms which may optionally contain one or more aromatic hydrocarbon radicals having from 6 to 10 carbon atoms or one or more heterocyclic radicals having from 5 to 14 carbon atoms; a di- or tri - valent radical comprising one or more optionally substituted aromatic hydrocarbon radicals having from 6 to 12 carbon atoms; or a heterocyclic di- or tri - valent radical having from 5 to 14 carbon atoms,

the mixture containing, on a basis of 100 parts by weight total, from 5 to 25 parts by weight of the bis- or *tris* - (5,6 - dihydro - 4H - 1,3 - oxazine) (B) to from 95 to 75 parts by weight of the acrylic resin (A).

2. A coating composition as claimed in claim 1, which also comprises one or more pigments and levelling agents.

3. A coating composition as claimed in claim 2, which comprises up to 150% by weight based on (A) and (B), of one or more pigments and from 0.1 to 5% by weight, based on (A) of a levelling agent.

4. A coating composition as claimed in any of claims 1 to 3, in which the acrylic resin (A) comprises:

I. from 25 to 70% by weight of styrene and/or α - methyl styrene;

II. from 30 to 65% by weight of an ester of acrylic acid or methacrylic acid having from 1 to 8 carbon atoms in the alcohol component or a mixture of two or more thereof, the methyl methacrylate content not being greater than 25% by weight; and

IV. from 5 to 20% by weight of acrylic acid and/or methacrylic acid.

5. A coating composition as claimed in any of claims 1 to 4, in which the *bis* - oxazine is 1,4 - *bis* - (5',6' - dihydro - 4'H - 1',3' - oxazin - 2' - yl) - benzene.

6. A coating composition as claimed in any of claims 1 to 5, in which the *bis* - oxazine is 1,3 - *bis* - (5',6' - dihydro - 4'H - 1',3' - oxazine - 2' - yl) - benzene.

7. A coating composition as claimed in any of claims 1 to 6, in which the *bis* - oxazine is 2,2' - *bis* - (5,6 - dihydro - 4H - 1,3 - oxazine).

8. A coating composition as claimed in any of claims 1 to 7 in which the *bis* - oxazine is 3,5 - *bis* - (5',6' - dihydro - 4'H - 1',3' - oxazin - 2' - yl) - pyridine.

9. A coating composition as claimed in any of claims 1 to 8, in which the *tris* - oxazine is 1,3,5 - *tris* - (5',6' - dihydro - 4'H - 1',3' - oxazin - 2' - yl) - benzene.

10. A coating composition substantially as

herein described with reference to any of the specific Examples.

11. A process for coating a metal article in which a powdered coating composition as claimed in any of claims 1 to 10 is applied to the article by an electrostatic spray process and the article is heated to a temperature in the range of from 130°C to 220°C to effect levelling and curing of the coating.

12. A process for coating a metal article substantially as herein described with reference to any of the specific Examples.

13. A coated article when prepared by a process as claimed in claim 11 or 12.

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